

Carbon-Carbon Aeroshell Chemical Reaction Model in an Open RPS in Martian Environment

Brad L Kirkwood, Christofer E. Whiting

October 2020



The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

Carbon-Carbon Aeroshell Chemical Reaction Model in an Open RPS in Martian Environment

Brad L Kirkwood, Christofer E. Whiting

October 2020

**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy**

**Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

Carbon-Carbon Aeroshell Reaction Model in Martian Environment for an Open RPS

Brad L. Kirkwood
**Idaho National Lab; Space Nuclear Power & Isotope
Technologies**

Christofer E. Whiting
**Univ. of Dayton Research Institute; Power & Energy
Division**

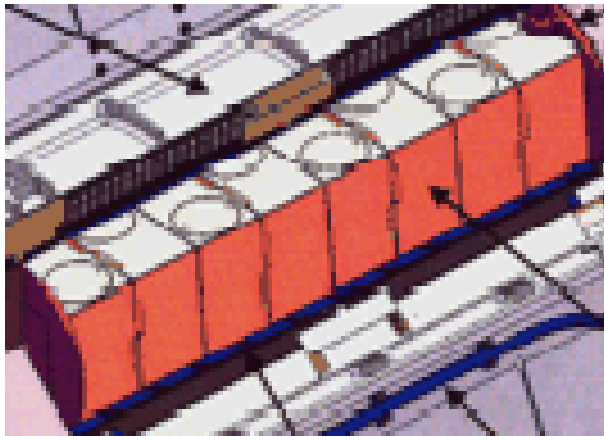
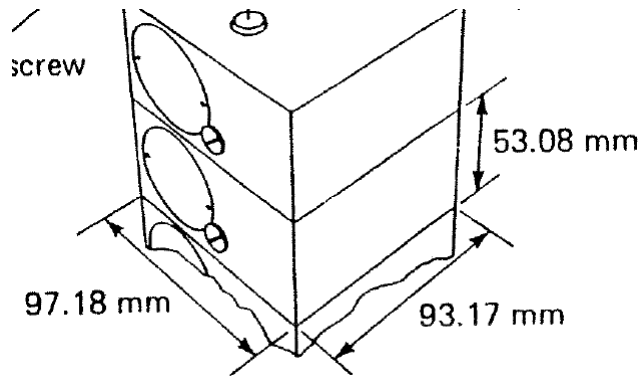
September 15, 2020

INL/EXT-20-59457 Rev. 2

**Space Nuclear Power
and Isotope Technologies**



FWPF Carbon-Carbon Aeroshell Reaction Model in Martian Environment



GPHS FWPF Carbon-Carbon Aeroshells

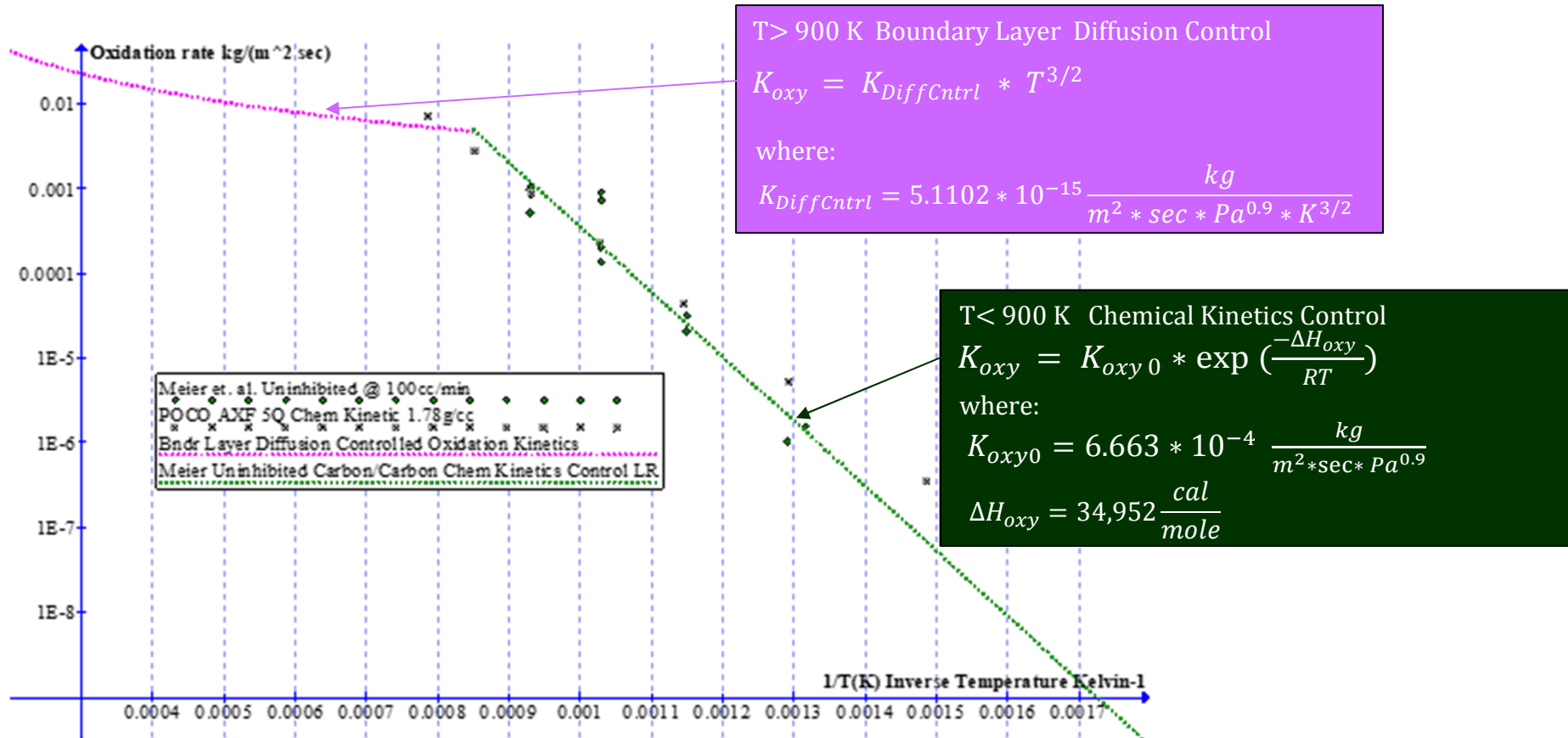
Create a Reaction Kinetics Model to Predict the Degree of Reaction and Life of a FWPF Carbon-Carbon Aeroshell in a Radioisotope Power System That Is Open to the Martian Environment. The Gas Reaction Kinetics Model Includes the Following Factors:

- The Kinetics of the Boudouard Reaction of CO_2 and Oxidation Reaction of O_2 with Carbon
- Temperature of Aeroshell In RPS
- Partial Pressure Chemistry of Martian Environment
- Internal and External Surface Area of C/C Aeroshell
- Growth of Internal Surface Area of C/C During Reaction

Space Nuclear Power
and Isotope Technologies



Oxidation Reaction Kinetics of Carbon-Carbon With O₂



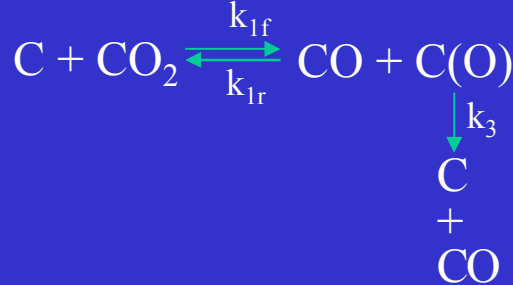
Arrhenius Plot of Oxidation Reaction of Uncoated, Uninhibited Carbon-Carbon at 21.3 kPa O₂

Data from J Cullinan, J. Schaeffer, E.A. Gulbransen, G.H. Meier, and F.S. Pettit, "Oxidation of Carbon-Carbon Composites and Coatings and Coatings on These Materials", Figure 24, AFOSR-TR-89-1643, Sept. 30, 1989, Air Force Office of Scientific Research Report, Bolling AFB, District of Columbia



Oxidation Reaction Kinetics Model of Carbon-Carbon

Boudouard Reaction of CO₂ with Carbon



Langmuir-Hinshelwood Kinetics Equation of Boudouard Reaction

$$k_{Boud} = \frac{K_{1*} p_{CO_2}}{1 + K_{2*} p_{CO} + K_{3*} p_{CO_2}}$$

Total C/C Reaction Kinetics Constant

$$K_{totalrxn} = \frac{K_{1*} p_{CO_2}}{1 + K_{2*} p_{CO} + K_{3*} p_{CO_2}} + K_{oxy} * p_{O_2}^n$$

where: $n = 0.9$

Degree of Reaction Equation

$$X(t) = 1 - \left[1 + \left[(m - 1) * \frac{K_{totalrxn}}{(1 - \varepsilon)} * Area_{Avg} * t \right] \right]^{\frac{1}{1-m}}$$

$$X = \frac{\Delta w}{w} \quad m = 2/3$$

The Total Boudouard Reaction of CO₂ with Carbon is a Combination of Two Intermediate Chemical Reactions

The Langmuir-Hinshelwood Kinetics Constants Were Derived From the Forward and Reverse Kinetics Constants of Intermediate Boudouard Reactions Measured by Hustad and Barrio

All Kinetics Constants Are Thermally Activated

The Total Reaction Kinetics Constant in the FWPF Reaction Model Adds the Kinetics of the Boudouard Reaction with the Oxidation Reaction

Area_{Avg} is the Average Internal And External Surface Area of Aeroshell

Definition of the Degree of Reaction Parameter



Increase of Carbon-Carbon Internal Surface Area During Reaction With Martian Environment

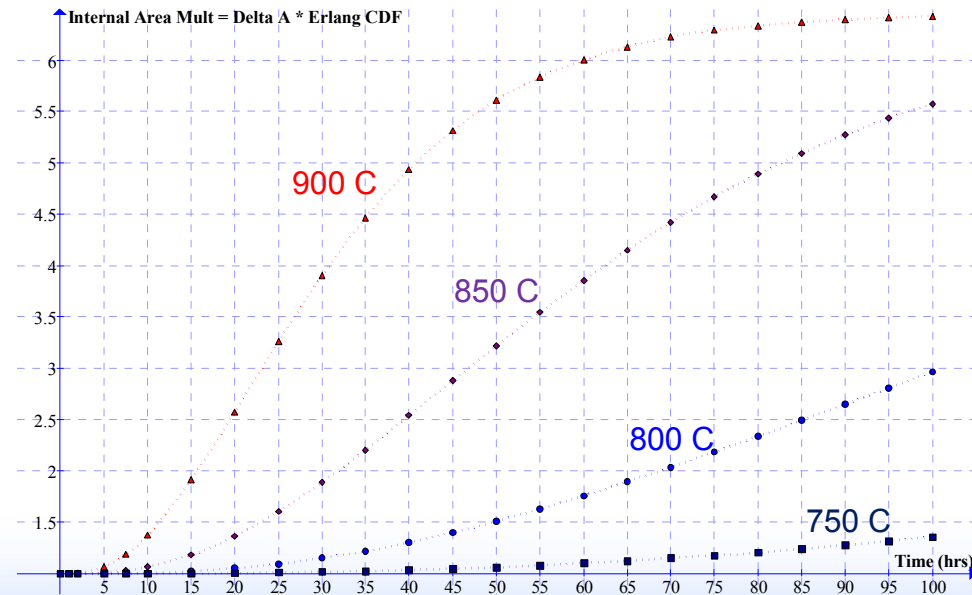
Oxidation Reaction Experiments on FWPF Carbon-Carbon in a Simulated Martian Gas Environment Were Performed by E.J. Opila



Opila's FWPF Carbon-Carbon Oxidation Reaction Specimen

Data from E.J. Opila, "Oxidation of Fine Weave Pierced Fabric Graphite in a Simulated Mars Environment at Temperatures Between 700 and 900 °C", NASA/TM-2006-214404, Oct. 2006, NASA Glenn Research Center Report, Cleveland Ohio

- The Internal Surface Area of the FWPF Carbon-Carbon Increased During the Oxidation Experiments
- The Internal Surface Area Increase Was Included in the FWPF Gas Reaction Model
 - S Shaped Erlang Cumulative Distribution Function of Time (shown)



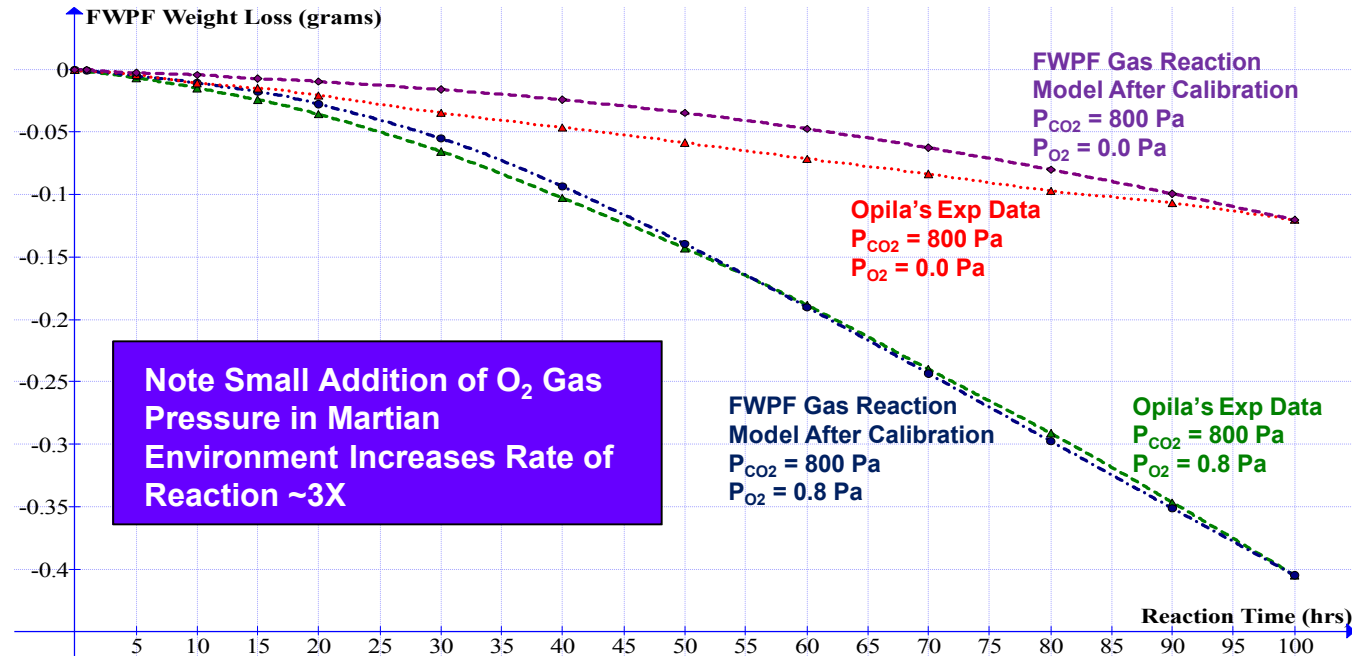
Calibration of the FWPF Gas Reaction Model in Martian Environment

The FWPF Gas Reaction Model was Calibrated With Opila's Experimental Weight Loss Data at 900 °C



Opila's FWPF Carbon-Carbon Oxidation Reaction Specimen

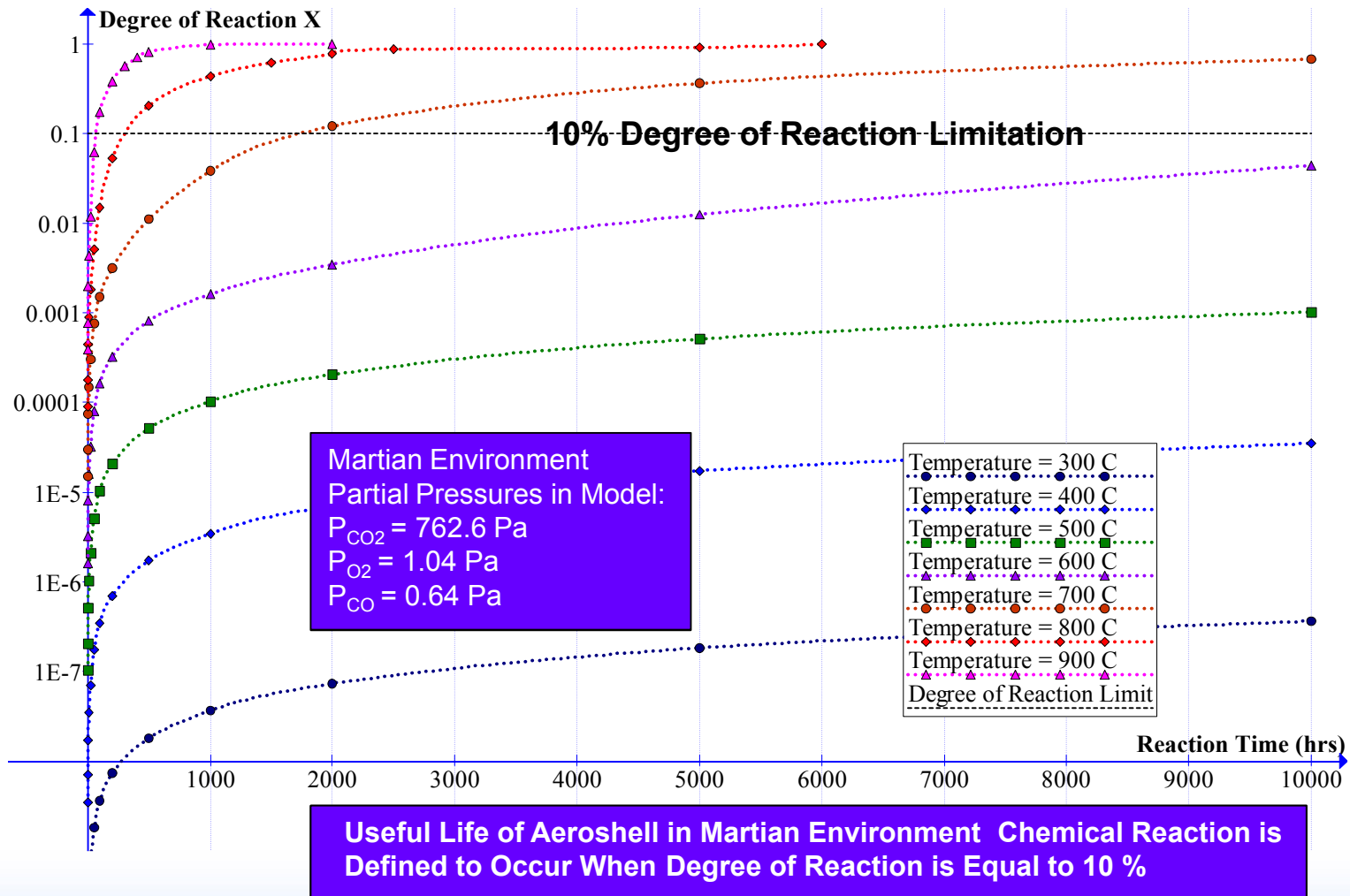
Data from E.J. Opila, "Oxidation of Fine Weave Pierced Fabric Graphite in a Simulated Mars Environment at Temperatures Between 700 and 900 °C", NASA/TM-2006-214404, Oct. 2006, NASA Glenn Research Center Report, Cleveland Ohio



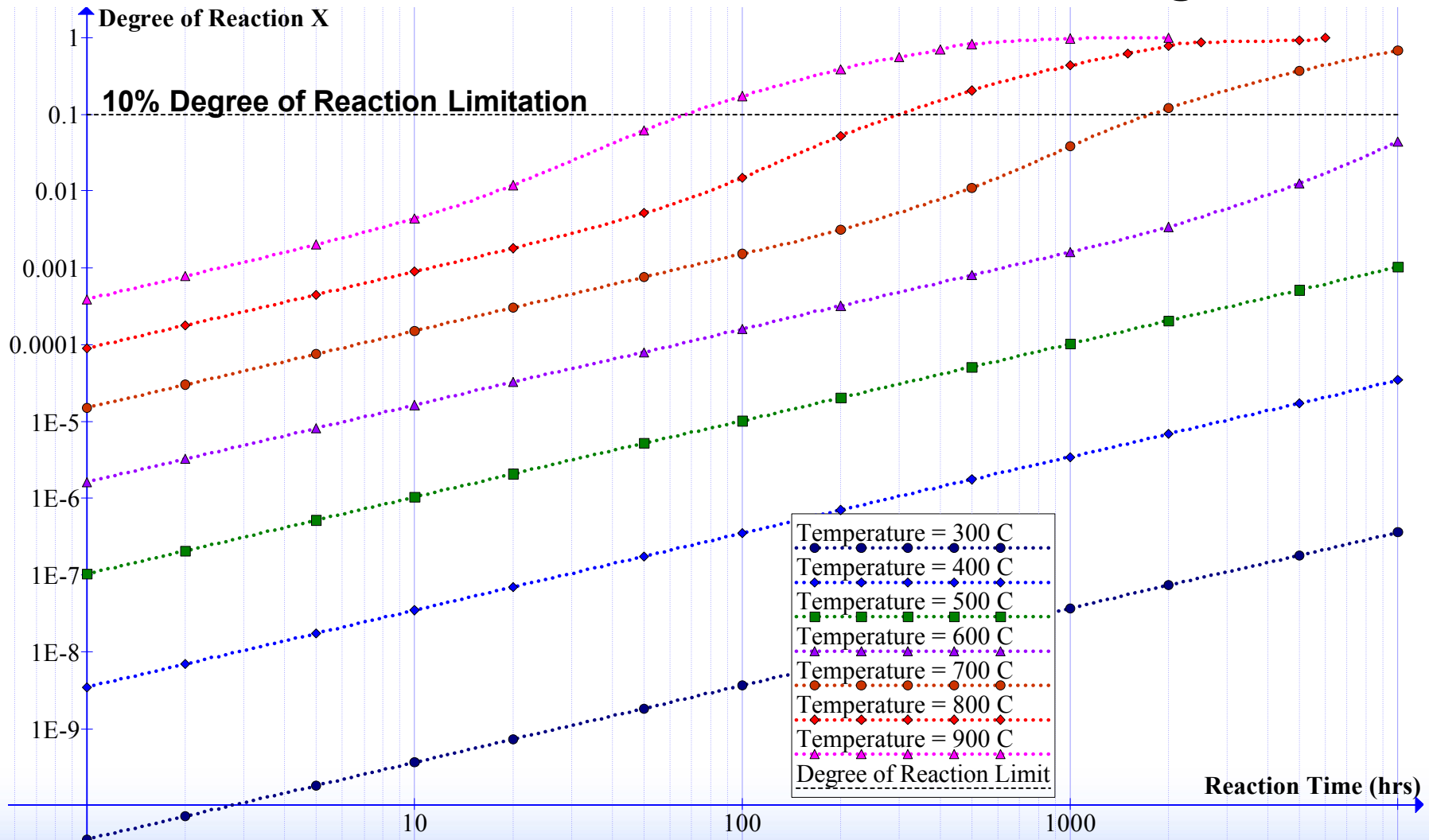
Boudouard Reaction Calibration Parameter	Oxidation Reaction Calibration Parameter	Calibration Parameter for Erlang CDF Rate Constant λ kg/(m ² * sec)	Oxidation Reaction Partial Pressure Exponent n	Erlang CDF Shape Parameter s	Erlang CDF Rate Constant λ
1.419×10^{-06}	3.424×10^{-04}	3.454×10^{-10}	0.9	3	1/12.0 hrs



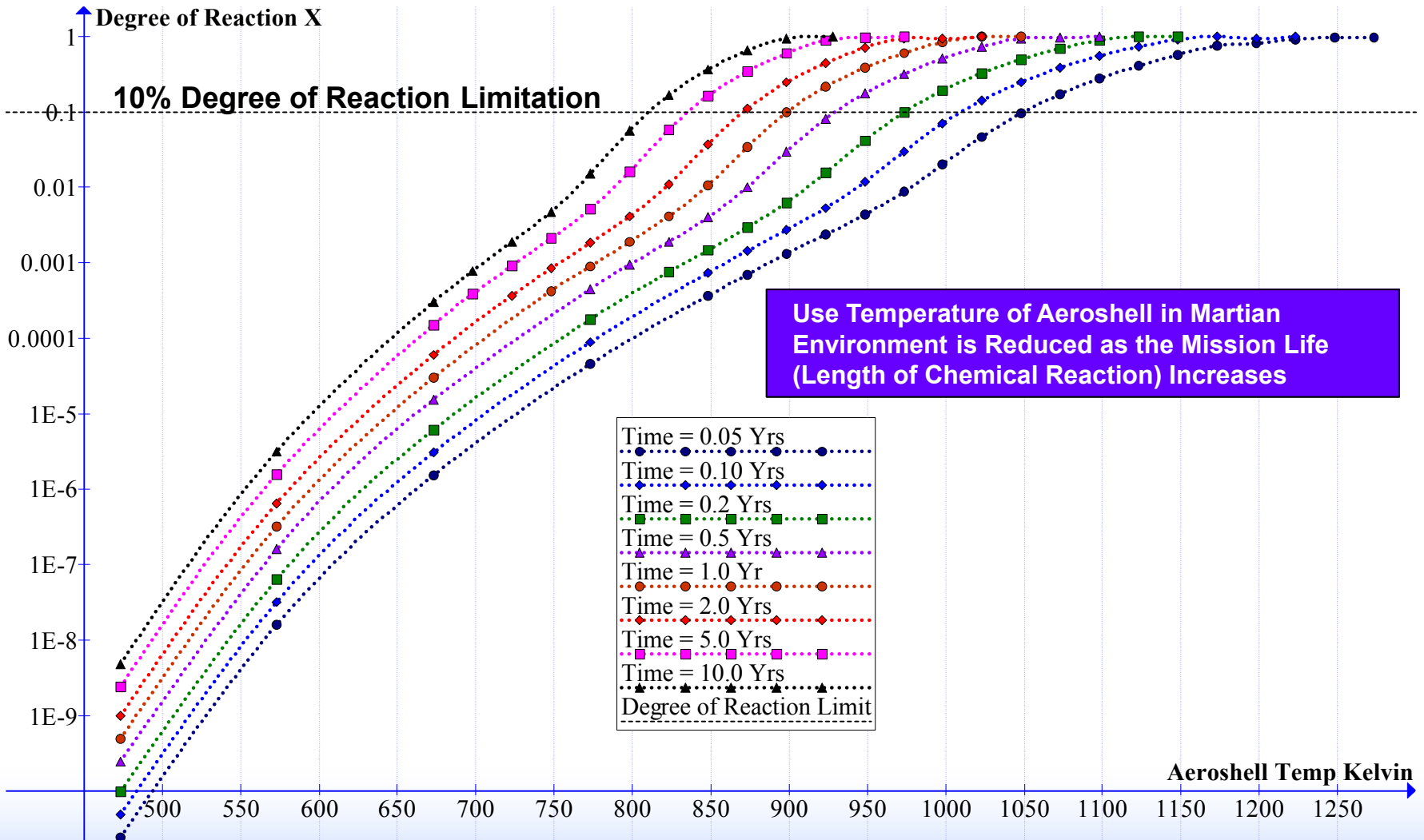
Predicted Degree of Reaction From FWPF Gas Reaction Model in Martian Environment: Regular Time



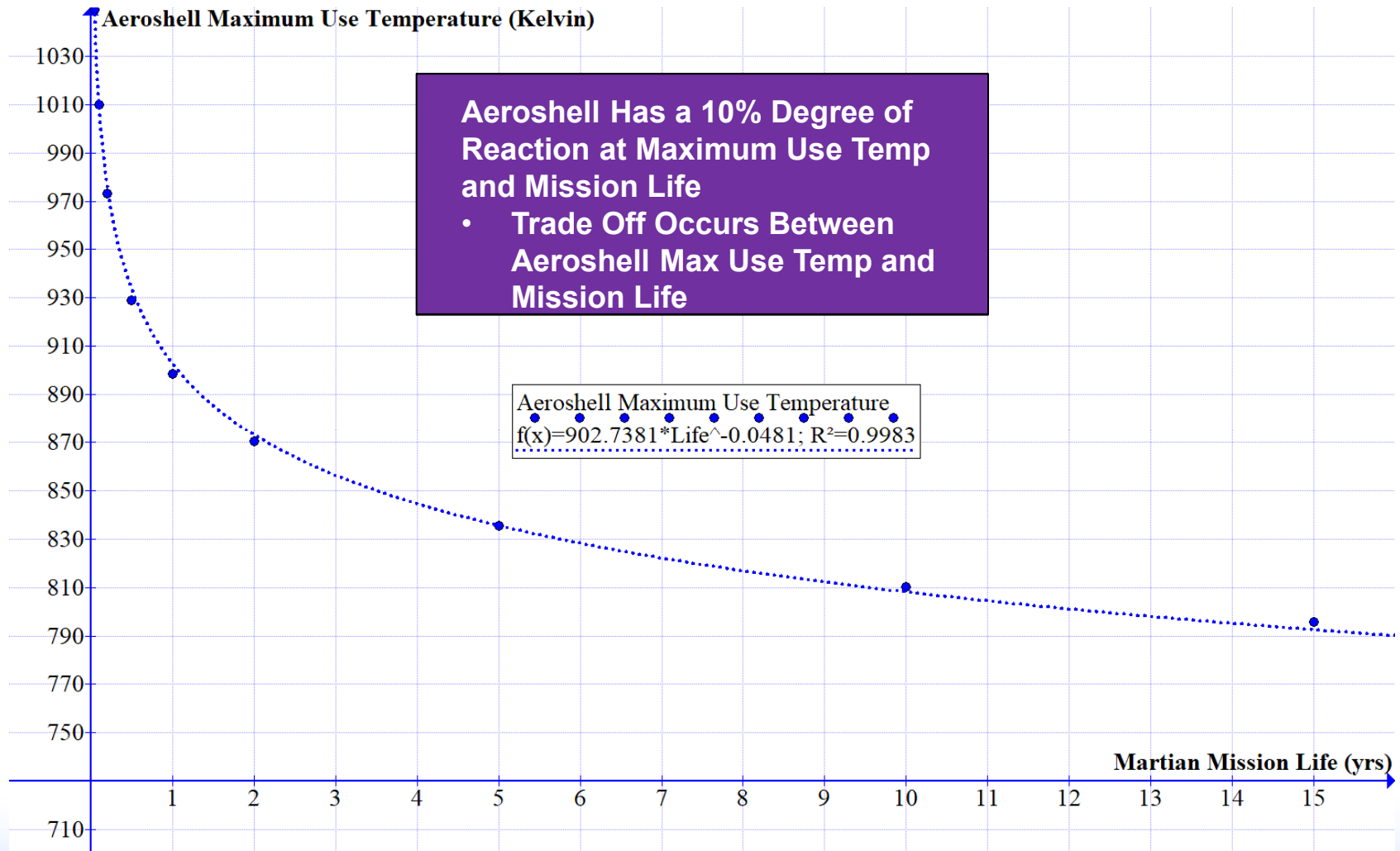
Predicted Degrees of Reaction From FWPF Gas Reaction Model in Martian Environment: Log Time



Predicted Degrees of Reaction From FWPF Gas Reaction Model in Martian Environment: Temperature



Max Use Temperature of GPHS Aeroshell in Open RPS in Martian Environment a Function of Mission Life

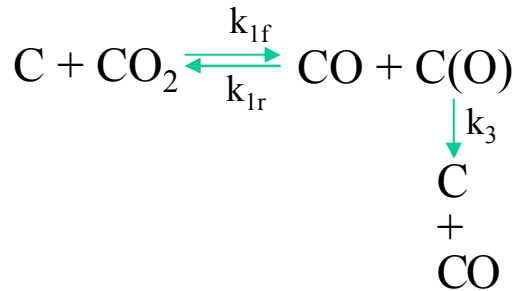


Summary

1. **A Chemical Kinetics Model was Developed to Predict the Degree of Chemical Reaction of FWPF Carbon-Carbon in a Martian Atmosphere. Model Considers the Following Factors:**
 - **The Boudouard Reaction of Carbon with CO_2 and the Oxidation Reaction with O_2 Gases in the Martian Environment**
 - **Partial Pressures of Gases in the Martian Environment**
 - **Temperature of the Aeroshell in the Radioisotope Power System**
 - **The Internal and External Surface Areas of the Carbon-Carbon Aeroshell**
 - **The Internal Surface Area Increases During the Reaction at High Temperatures**
2. **Model is Applicable to Radioisotope Power Systems That Are Open to the Environment.**
3. **Model Was Calibrated with Opila's Experimental Measurements of FWPF Carbon-Carbon in a Martian Environment to Improve its Predictive Capability.**
4. **Degree of Reaction in Aeroshell Was Limited to 10% at Mission Lifetime, Before Structural Integrity and Thermal Conductivity Would be Substantially Degraded**
5. **Results of the Model Show That a Trade Off Occurs Between the Maximum Allowable Aeroshell Temperature and the Desired Mission Life**
 - **Maximum Aeroshell Temperatures Limited to Less Than 830 Kelvin for a Mission Life on Mars of 5+ Years**



Kinetics of Boudouard Reaction of Carbon with CO₂



$$k_{\text{Boud}} = \frac{K_1 * p_{\text{CO}_2}}{1 + K_2 * p_{\text{CO}} + K_3 * p_{\text{CO}_2}}$$

Langmuir-Hinshelwood Kinetics Equation

$$k_{1f} = k_{1fo} * \exp(-\Delta H_1 / (R * T))$$

$$k_{1r} = k_{1ro} * \exp(-\Delta H_2 / (R * T))$$

$$k_3 = k_{3o} * \exp(-\Delta H_3 / (R * T))$$

Thermally Activated Rate Constants of Boudouard Reaction (Hustad & Barrio)

$$K_1 = k_{1fo} * \exp(-\Delta H_1 / (R * T))$$

$$K_2 = k_{1ro} / k_{3o} * \exp(-(\Delta H_2 - \Delta H_3) / (R * T))$$

$$K_3 = k_{1fo} / k_{3o} * \exp(-(\Delta H_1 - \Delta H_3) / (R * T))$$

Langmuir-Hinshelwood Kinetics Constant Equations

Data from M Barrio and J. E. Hustad, "CO₂ Gasification of Birch Char and the Effect of CO Inhibition on the Calculation of Chemical Kinetics", Progress in Thermochemical Biomass Conversion, April 2008, pp. 47-60

- The Boudouard Reaction of CO₂ with Carbon is a Combination of Two Intermediate Reactions as Shown. In the Second Reaction an Oxygen Atom is Absorbed to a Carbon Atom and Reacts to Form Carbon Monoxide. The Reaction Equations Show the Forward and Reverse Kinetics Constants

- The Total Boudouard Reaction Rate was Modelled Using a Langmuir-Hinshelwood Kinetics Equation. This Kinetics Equation Causes the Reaction Rate of the Boudouard Reaction to go to Zero as the CO Increases in a Closed System

- The Langmuir-Hinshelwood Kinetics Constants Are Derived From the Forward and Reverse Kinetics Constants of the Two Intermediate Reactions Measured by Hustad and Barrio

Hustad and Barrio Boudouard Reaction Rate Constants	Hustad and Barrio Boudouard Reaction Rate Activation Energies
$k_{1fo} = 1.30 / \text{Pa} \cdot \text{s}$	$\Delta H_1 = 165 \text{ KJ/mol}$
$k_{1ro} = 3.6 \times 10^{-6} / \text{Pa} \cdot \text{s}$	$\Delta H_2 = 20.8 \text{ KJ/mol}$
$k_{3o} = 3.23 \times 10^7 / \text{s}$	$\Delta H_3 = 236 \text{ KJ/mol}$
Langmuir-Hinshelwood Coefficients	Langmuir-Hinshelwood Activation Energies
$K_{1o} = k_{1fo} = 1.30 / \text{Pa} \cdot \text{s}$	$\Delta H_1 = 165 \text{ KJ/mol}$
$K_{2o} = k_{1ro} / k_{3o} = 1.1145 \times 10^{-13} / \text{Pa}$	$\Delta H_2 - \Delta H_3 = -215.2 \text{ KJ/mol}$
$K_{3o} = k_{1fo} / k_{3o} = 4.0248 \times 10^{-8} / \text{Pa}$	$\Delta H_1 - \Delta H_3 = -71 \text{ KJ/mol}$

Space Nuclear Power
and Isotope Technologies



Derivation of the Degree of Reaction of the Carbon-Carbon Aeroshell

$$X = \frac{\Delta w}{w} \quad \text{Definition of the Degree of Reaction Parameter X}$$

$$\frac{dX}{dt} = K_{total\ rxn} * A(t) * \frac{(1 - X)^m}{(1 - \varepsilon)} \quad \text{1st Order Differential Equation of the Degree of Reaction}$$

Where: Δw is weight lost of aeroshell during reaction
 m is shape parameter
 $m = 1$ Volume Reaction Model
 $m = 1/2$ cylindrical particles like graphite fibers
 $m = 2/3$ spherical particles like carbon matrix
 $m = 0$ flat plate particles
 $A(t)$ = Total Internal + External Surface Area as a Function of Time
 ε = Initial Porosity of Carbon - Carbon

$$X(t) = 1 - \left[1 + \left[(m - 1) * \frac{K_{total\ rxn}}{(1 - \varepsilon)} * \int_0^t A(t) * dt \right] \right]^{\frac{1}{1-m}} \quad \text{Solution of the Degree of Reaction as a Function of Time for } m \neq 1$$

$$X(t) = 1 - \exp \left[- \left[\frac{K_{total\ rxn}}{(1 - \varepsilon)} * \int_0^t A(t) * dt \right] \right] \quad \text{Solution of the Degree of Reaction as a Function of Time for } m = 1 \text{ Volume Reaction Model}$$

P. Lahijani, Z.A.Zainal, M. Mohammadi, and A.R. Mohamed; "Conversion of Greenhouse Gas CO₂ to Fuel Gas CO Via the Boudouard Reaction: A Review"; Renewable and Sustainable Energy Reviews, Vol. 41 (2015) pp. 615-632



Insertion of Erlang CDF Surface Area Increase Into Degree of Reaction Equation

The Integral of the Internal Surface Area With Time $\int_0^t A(t) * dt = A_0 t + \Delta A \int_0^t cdf(t) * dt$

Insertion of the Internal Surface Area Integral into the Degree of Reaction Equation
$$X(t) = 1 - \left[1 + \left[(m - 1) * \frac{K_{total}}{(1 - \varepsilon)} * \left(A_0 t + \Delta A * \int_0^t cdf(t) * dt \right) \right] \right]^{\frac{1}{1-m}}$$

The Integral of the Erlang Cumulative Distribution Function With Time
$$\int_0^t cdf(t) * dt = \int_0^t \left[1 - \sum_{n=0}^{s-1} \frac{1}{n!} * (\lambda * t)^n * \exp(-\lambda * t) \right] * dt$$

$$Area_{Avg} = \frac{A_0 t + \int_0^t cdf(t) * dt}{(t - 0)} = A_0 + \frac{\Delta A}{(t - 0)} \left[t + \left[\frac{1}{\lambda} \exp(-\lambda t) - 1 \right] + \left[\lambda \exp(-\lambda t) * \left[\frac{1 + \lambda t}{\lambda^2} \right] - \frac{1}{\lambda} \right] + \left[\exp(-\lambda t) \left[\frac{\lambda * t^2}{2} + t + \frac{1}{\lambda} \right] - \frac{1}{\lambda} \right] \right]$$

Final Degree of Reaction Equation
$$X(t) = 1 - \left[1 + \left[(m - 1) * \frac{K_{total}}{(1 - \varepsilon)} * Area_{Avg} * t \right] \right]^{\frac{1}{1-m}}$$



Increase of Carbon-Carbon Internal Surface Area During Reaction With Martian Environment

Oxidation Reaction Experiments on FWPF Carbon-Carbon in a Simulated Martian Gas Environment Were Performed by E.J. Opila



Opila's FWPF Carbon-Carbon Oxidation Reaction Specimen

Data from E.J. Opila, "Oxidation of Fine Weave Pierced Fabric Graphite in a Simulated Mars Environment at Temperatures Between 700 and 900 °C", NASA/TM-2006-214404, Oct. 2006, NASA Glenn Research Center Report, Cleveland Ohio

- The Internal Surface Area of the FWPF Carbon-Carbon Was Measured by BET Surface Analysis to Increase By a Factor of 6.45 During the Experiments
- The Surface Increase Was Included in the FWPF Gas Reaction Model as a Function of Time Using an S Shaped Erlang Cumulative Distribution Function
 - The Erlang Cumulative Distribution Shape Factor $s = 3$ (Curve Fit to Opila's Data)
 - The Erlang Rate Parameter λ Was Modelled to be Proportional to the Total Reaction Rate Parameter, $K_{totalrxn}$

